

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 670 916 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
27.08.1997 Bulletin 1997/35

(21) Application number: **94900026.9**

(22) Date of filing: **26.11.1993**

(51) Int Cl.⁶: **C25D 5/18, C25D 3/12**

(86) International application number:
PCT/CA93/00492

(87) International publication number:
WO 94/12695 (09.06.1994 Gazette 1994/13)

(54) **NANOCRYSTALLINE METALS**
NANOKRISTALLINE METALLE
METAUX NANOCRISTALLINS

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI NL PT SE

(30) Priority: **30.11.1992 US 983205**

(43) Date of publication of application:
13.09.1995 Bulletin 1995/37

(73) Proprietor: **QUEEN'S UNIVERSITY AT KINGSTON**
Kingston Ontario K7L 3N6 (CA)

(72) Inventors:
• **ERB, Uwe**
Glenburnie, Ontario K0H 1S0 (CA)
• **EL-SHERIK, Abdelmounam M.**
Kingston, Ontario K7L 1S3 (CA)

• **CHEUNG, Cedric K.S.**
Kingston, Ontario K7K 6K8 (CA)
• **AUS, Martin J.**
Kingston, Ontario K7K 6K6 (CA)

(74) Representative: **Johnson, Terence Leslie et al**
Edward Evans & Co.
Chancery House
53-64 Chancery Lane
London WC2A 1SD (GB)

(56) References cited:
WO-A-92/15998 DE-A- 2 555 834
GB-A- 2 236 763

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 670 916 B1

Description

Field of Invention

This invention relates to nanocrystalline metals and alloys thereof and methods of production thereof, and more particularly to the production of nanocrystalline nickel having a grain size of less than 11 nanometers and selected pure metals, binary, ternary and quaternary alloys thereof having a grain size of less than about 100 nanometers.

Background of Invention

Nanocrystalline materials are a new class of disordered solids which have a large volume fraction (up to 50% or more of the atoms) of defect cores and strained crystal lattice regions. The physical reason for the reduced density and the non-lattice spacing between the atoms in the boundary cores is the misfit between the crystal lattice of different orientation along common interfaces. The nanocrystalline system preserves in the crystals a structure of low energy at the expense of the boundary regions which are regions at which all of the misfit is concentrated so that a structure far away from equilibrium is formed (Gleiter, *Nanocrystalline Materials*, Prog. in Matls Science, Vol 33, pp 223-315, 1989). A structure of similar heterogeneity is not formed in thermally induced disordered solids such as glasses. Nanocrystalline materials typically have a high density (10^{19} per cm^3) of grain interface boundaries. In order to achieve such a high density, a crystal of less than about 100 nm diameter is required. Over the past few years great efforts to make smaller and smaller nanocrystals, down to about 10 nm have been made. It would appear, however, that the properties of even smaller nanocrystals (less than 10 nm) offer significant advantages over larger nanocrystals, particularly in the area of hardness, magnetic behaviour hydrogen storage, and wear resistance.

Nanocrystalline materials, which are also known as ultrafine grained materials, nanophase materials or nanometer-sized crystalline materials, can be prepared in several ways such as by sputtering, laser ablation, inert gas condensation, oven evaporation, spray conversion pyrolysis, flame hydrolysis, high speed deposition, high energy milling, sol gel deposition, and electrodeposition. Each of these methods has its special advantages and disadvantages and not all methods are suitable for all types of nanocrystalline materials. It is becoming apparent, however, that electrodeposition is the method of choice for many materials. The major advantages of electrodeposition include (a) the large number of pure metals, alloys and composites which can be electroplated with grain sizes in the nanocrystalline range, (b) the low initial capital investment necessary and (c) the large body of knowledge that already exists in the areas of electroplating, electrowinning and electroforming.

Using electrodepositing techniques, nanocrystalline electrodeposits of nickel and other metals and alloys have been produced over the years with ever smaller diameters down to the 10-20 nm range. Heretofore, it has not been possible to get sizes below about 10 nm diameter. Small crystal sizes increase the proportions of grain boundaries and triple junctions in the material. It is known that room temperature hardness increases with decreasing grain size in accordance with the known Hall-Petch phenomenon. However, it has now been determined that as the number of triple junctions in the material increases, at about 30 nm down, there is a deviation from normal Hall-Petch behaviour and hardness does not continue to increase as the grain size falls below a critical value. Indeed, it has now been shown that in pure nickel nanocrystalline materials the hardness reaches a peak in the 8-10 nm range. Other materials even show a decrease in hardness as the grain size decreases below about 10 nm.

Binary nickel-iron nanocrystalline alloys have been described in a University of California Ph.D. thesis by D.L. Grimmer in 1990. Nickel-Phosphorus and Cobalt-Tungsten nanocrystalline materials are also known (C. McMahon et al *Microstr. Sci.* 17, 447 (1989) and Erb et al *Nanostructured Mats Vol 2* 383-390 (1993)).

Nanocrystalline materials have improved magnetic properties compared to amorphous and conventional polycrystalline materials. Of particular importance is the saturation magnetization, which should be as high as possible regardless of grain size. However, previous studies on gas-condensed nanocrystalline nickel (Gong et al, *J. Appl. Phys* 69, 5119, (1991)) reported decreasing saturation magnetization with decreasing grain size. It would appear, however, that this phenomenon is associated with the method of production as electrodeposited nanocrystalline nickel in accordance with the present invention shows little change in saturation magnetization.

An object of the present invention is to provide a novel pulsed electrodeposition process for making nanocrystalline materials of less than 100 nm in diameter.

According to one aspect of the invention there is provided a process for electrodepositing a selected metallic material in nanocrystalline form on a substrate in which an aqueous, electrolyte containing ions of said selected metallic material is introduced into an electrolytic cell having an anode and a cathode, while maintaining said electrolyte at a temperature in the range between about 15° and about 75°C, characterised by passing a D.C. current, having a peak current density in the range between about 0.1 and about 3.0 A/cm², at pulsed intervals during which said current passes for a time period in the range of about 0.1 to about 50 milliseconds and does not pass for a time period in the range of about 1 to about 500 milliseconds, between said anode and said cathode so as to deposit said selected metallic material in nanocrystalline form and having a grain size of less than 100 nm on said cathode.

The process hereinbefore defined may preferably

by characterised by maintaining said electrolyte at a temperature in the range between about 55° and about 75°C and may be further characterised in that said peak current density is in the range between about 1.0 and 3.0/A/cm², at pulsed intervals during which said current passes for a time period in the range of about 1.0 to about 5 milliseconds and does not pass for a time period in the range of about 30 to 50 milliseconds.

According to a second aspect of the invention there is provided a nanocrystalline nickel material, characterised by an average grain size of less than 11 nanometres and by a hardness which is at a maximum in a size range of 8 - 10 nm, and by saturation magnetization properties substantially equal to those of said nickel material in normal crystalline form.

According to a third aspect of the invention there is provided a nanocrystalline metallic material having a grain size of less than 100 nm characterised by being selected from the group consisting of (a) pure metal selected from the group consisting of Co, Cr, Cu and Fe, and (b) alloys containing at least two elements selected from Ni, Fe, Co, Zn, Ti, S, Mg, W, Cr, Cu, Mo, Mn, V, Si, P, C, and S, with the proviso that, in a binary alloy when a first said element is nickel, the second element is not iron or phosphorus, and in a binary alloy in which the first element is Co, the second element is not W.

According to a fourth aspect of the invention there is provided a nanocrystalline ternary or quaternary nickel-iron alloy having a grain size of less than 100 nm and characterized in that it is of the Ni Fe X₁ X₂ type where X₁ and X₂ are the same or different and selected from the group consisting of Cr, Co, Cu, Mo, Mn, V, Ti, Mg, Si, P, C, and S.

Brief Description of Drawings

Figure 1 is a diagrammatic sketch of one embodiment of an apparatus for use in the process of the present invention;

Figure 2 is a graph illustrating current density versus time during a plating cycle;

Figure 3 is a graph of hardness (VHN) versus grain size for nanocrystalline nickel (Hall Petch plot);

Figure 4 is a graph of magnetic saturation (emu/g) versus grain size for nanocrystalline nickel produced according to the present invention, and compared to the prior art;

Figure 5 is a diagrammatic sketch of an alternative embodiment of an apparatus for use in the present invention;

Figure 6 is a graph illustrating composition of ternary Ni Fe Cr alloys produced in baths containing different concentrations of chromium;

Figure 7 is a graph illustrating resistivity of nanocrystalline nickel as a function of grain size;

Figure 8 is a graph illustrating excess resistivity as a function of intercrystalline volume fraction; and

Figure 9 shows polarization curves for nano- and

poly-crystalline nickel.

Detailed Description of Preferred Embodiments

As noted hereinabove pulsed direct current electrodeposition has been found to produce superior nanocrystalline materials, and particularly nickel, having a grain size of less than about 11 nm. Ternary or quaternary nickel-iron alloys having a grain size of less than about 100 nm can also be produced by pulsed D.C. electrodeposition or by D.C. electroplating as well as nanocrystalline Co, Cr, Cu and Fe.

The invention will now be described with particular reference to the production of nanocrystalline nickel and Figure 1 is a sketch showing a laboratory apparatus for carrying the present invention into practice. A plating cell 1, generally of glass or thermoplastic construction, contains an electrolyte 2 comprising an aqueous acid solution of nickel sulfate, nickel chloride, boric acid and selected grain size inhibitors, grain nucleators and stress relievers, to be described in more detail hereinbelow. An anode 3 is connected to an ammeter 4 (Beckman, Industrial 310) in series connection to a conventional DC Power Source 5 (5 amp, 75 volt max output). The anode may be any dimensionally stable anode (DSA) such as platinum or graphite, or a reactive anode, depending on the material desired to be deposited. Preferably, in the case of nickel deposition, the anode is an electrolytic nickel anode. A cathode 6 is connected to the power source 5 via a transistored switch 7. Cathode 6 may be fabricated from a wide variety of metals such as steel, brass, copper and or nickel, or non-metal such as graphite. Preferably, cathode 6 is fabricated from titanium to facilitate stripping of the nickel deposited thereon. Switch 7 is controlled by a wave generator 8 (WaveTEK, Model 164) and the wave form is monitored on an oscilloscope 9 (Hitachi V212).

The temperature of the electrolyte 2 is maintained in the range between about 55 and 75° C by means of a constant temperature bath 10 (Blue M Electric Co.). A preferred temperature range is about 60-70° C and most preferably about 65° C. The pH is controlled by additions such as Ni₂CO₃ powder or 7:1 H₂SO₄: HCl as required.

The quality of the deposit and the crystalline structure thereof are functions of the peak current density in the cell 1, and the rate of pulsing the current. Figure 2 illustrates the maximum current density (I_{peak}) as a function of time. It will be noted that generally the time off (t_{off}) is longer than the time on (t_{on}) and that the current density I_{peak} may vary between about 1.0A/cm² and about 3.0A/cm². The t_{on} may vary between about 1.0 and 5.0 msec., with a preferred range of 1.5 - 3.0 msec and an optimum value of 2.5 msec. The t_{off} may range from about 30 msec. to 50 msec. with an optimum of 45 msec. It will be appreciated that I_{peak} , t_{on} and t_{off} are interrelated and may be varied within the stated ranges. If the I_{peak} is too high, there is a risk that the deposited material will burn and, if too low, the grain size will in-

crease.

In all of the following examples, which are illustrative only and not limiting on the invention, the electrolytic cell described above was employed with an electrolytic nickel anode and a titanium cathode and an aqueous electrolyte (Bath 1) containing:

Nickel Sulphate (BDH)	300 gm/l
Nickel Chloride (BDH)	45 gm/l
Boric Acid (BDH)	45 gm/l

in distilled water. The pH was adjusted, as noted above, by addition of Ni_2CO_3 powder or 7:1 H_2SO_4 : HCl. The temperature was maintained at 65° C, for a standard plating time of 3 hours. Saccharin is a known stress reliever and grain refining agent and may be added in amounts up to about 10 gm/l. Other stress relievers and grain refining agents which may be added include coumarin sodium lauryl sulfate and thiourea. If the bath temperature rises, it may be desirable to add a grain size inhibitor such as phosphorous acid in relatively small amounts up to about 0.5 - 1 gm/l.

Example 1

Using the apparatus described with reference to Figure 1 and a basic bath electrolyte composition described above as "Bath 1", 0.5 gm/l saccharin (Aldrich) was added and the pH adjusted to pH 2. The I_{peak} was 1.9 A/cm² and t_{on} was 2.5 m sec. and t_{off} was 45 m sec. The result was a porosity free nanocrystalline nickel deposit of 0.250 - 0.300 mm thickness with an average grain size of 35 nm.

Example 2

The procedure and operating conditions of Example 1 were repeated except that the saccharin concentration was increased to 2.5 gm/l. The result was a porosity free deposit of 0.220 - 0.250 mm thickness with an average grain size of 20 nm.

Example 3

Example 1 was repeated except that the saccharin concentration was increased to 5 gm/l. The result was a porosity free deposit of 0.200 mm thickness with an average grain size of 11 nm.

Example 4

Example 1 was repeated except that the pH was adjusted to pH 4.5 and the saccharin concentration was increased to 10 gm/l. The result was a porosity free deposit of 0.200 - 0.220 mm- thickness with an average grain size of 6 nm.

Example 5

The products of Examples 1-3 were subjected to hardness testing using a standard Vickers hardness technique. The results are tabulated in Figure 3 and illustrate that at the large grain sizes porosity free electroplated nickel nanocrystals obey the well established Hall-Petch relationship, i.e. increasing hardness with decreasing grain size. However, for the very small sizes of the present invention there is a clear deviation from the Hall-Petch relationship indicating a maximum hardness in the 8 - 10 nm size range.

Example 6

The saturation magnetization of the products of Examples 1-3 was measured using conventional methods. The results are tabulated in Figure 4 and compared with the saturation magnetization of gas condensed nanocrystalline nickel as reported by Gong et al, supra. It will be noted that while Gong et al report decreasing saturation magnetization with decreasing grain size, the products of the present invention show very little change in saturation magnetization with grain size variation, and even at the smallest grain sizes it is essentially the same as for conventional nickel.

The nanocrystalline materials of this invention, and particularly nanocrystalline nickel can be used to provide hard, wear resistant coatings on many surfaces. They can also be used as hydrogen storage materials, as catalysts for hydrogen evolution and as magnetic materials.

While the invention has been described thus far with reference particularly to nanocrystalline nickel, the principles thereof are equally applicable to nanocrystalline soft magnet materials, which are frequently ternary and quaternary iron-nickel alloys, and more particularly include Permalloy® (78.5 Ni 17.1 Fe 3.8 Cr 0.6 Mn), Hy Mu® (80 Ni 16 Fe 4 Mo) Superalloy® (79 Ni 15.7 Fe 5 Mo 0.3 Mn) and Mumetal (76 Ni 17 Fe 5 Cu 2 Cr) (Woldman, Engineering Alloys, 4th Ed, 1962). Other ternary and quaternary alloys may contain elements selected from Ni, Fe, Co, Zn, W, Cr, Cu, Mo, Mn, V, Ti, Mg, Si, P, C and S. The soft magnetic materials find utility in many applications but are particularly useful for recording head applications which require high electrical resistivity to improve high frequency permeability and to minimize eddy current losses. These materials also exhibit good wear characteristics. It has also been found that, while useful, pulsed D.C. electroplating is not essential for the production of nanocrystalline (<50 nm) nickel-iron alloys such as those described above. D-C electroplating under carefully controlled conditions has been found adequate.

Example 7 Production of Ternary Nickel-Iron Chromium Alloys

A simple laboratory electroplating bath 51 (Fig. 5) was placed on a heating plate 52. An anode 54, preferably but not essentially, graphite and a metallic, preferably copper, cathode 55 were immersed in an electrolyte solution 56 in bath 51 and connected to a controlled DC power supply 53. The electrolyte comprised an aqueous solution containing (in grams/litre of solution):

NiCl ₂ · 6H ₂ O	50
CrCl ₃ · 6H ₂ O	0 - 100
FeCl ₂ · 4H ₂ O	1
NaCl	0 - 50
B(OH) ₃	25
NH ₄ Cl	25

The bath temperature was maintained at a temperature between about 15°C and about 50°C (preferably room temperature) and the pH of the bath was maintained in the range 1-3, depending on the chromium content. At high chromium levels the pH was lowered to prevent formation of chromium hydroxide. The current density was maintained at about 50 mA/sq cm of cathode for periods of time up to about 2 hours with continuous stirring (0-500 rpm).

In an alternative embodiment using a pulsed D.C. electrolytic cell, periodic pulse reversal was practised resulting in some grain size reduction and improved surface quality. Quality may also be improved using the stress relievers previously described and in addition sodium citrate, EDTA, citric acid or sodium fluoride.

The composition of the alloy deposited on the copper cathode was analyzed by energy dispersive x-ray spectroscopy and the results, in terms of the chromium concentration of the bath were plotted in Figure 6. It will be noted that the chromium content of the alloy is substantially constant at about 1% but the nickel content tends to fall from a maximum of about 86% at 0 g/l Cr in the bath to a minimum of about 78% at a concentration of 50 g/l Cr in the bath. Scanning electron microscopy indicated that the grain size of the alloy product was less than 100 nanometres while x-ray diffraction studies indicated a grain size of about 10-15 nanometres with some grain sizes up to about 37 nm.

The electrical, mechanical and magnetic properties of the pure nanocrystalline nickel products of Examples 3 and 4 have been studied in some detail, and it has been determined, somewhat surprisingly in view of previously published results (Gong et al J. Appl. Phys. 69, 5119 (1991)) that saturation magnetization (Ms) of nanocrystalline nickel produced by the process of examples 2, 3 and 4 is essentially independent of grain size. This is, however, consistent with recent calculations (Szpunar et al, Condensed Matter Physics, in press) that show that the magnetic moment of atoms located

in special high angle grain boundaries is only insignificantly reduced. Even in an amorphous structure the reduction in Ms is less than 20% and for 10nm grain sizes with an intercrystalline volume fraction of 27%, the overall reduction in Ms is less than 5%.

Coercivity (Hc) of 50nm nanocrystalline nickel is about 2.0 kA/m which is about 50% lower than that of conventional polycrystalline (100 nm plus) material (3.0 kA/m). Further reduction in grain size results in an increase in coercivity back to the level of the polycrystalline material, which is believed due to the transition from multidomain to single domain grains.

Figure 7 shows that the room temperature electrical resistivity of the material with a grain size of 11nm is increased by a factor of three over the resistivity value observed for conventional polycrystalline material. At lower temperatures this factor increases to approximately five times. This behaviour can be understood in terms of electron scattering at the grain boundaries and triple junctions in the material which should result in an increase in resistivity with increasing intercrystalline volume fraction. This is demonstrated in Figure 8 which shows the excess resistivity as a function of the intercrystalline volume fraction for the grain sizes shown in Figure 7. The excess resistivity is defined here as the total resistivity minus the resistivity of conventional polycrystalline nickel for which the intercrystalline volume fraction is negligible. The intercrystalline volume fractions in Figure 8 were derived for a grain boundary thickness of 1nm.

Reduced grain size usually results in increased hardness as a result of Hall-Petch strengthening. The Hall-Petch graph for electrodeposited Ni is shown in Figure 3. Although there is deviation from linearity for grain sizes less than 30nm the important finding is that the hardness of the material is increased by a factor of 5 when reducing the grain size from 100µm to 10nm.

Using pin-on-disk wear testing under dry conditions an enhancement of the wear resistance by a factor of four was observed for the same materials.

The corrosion behaviour of nanocrystalline electrodeposits has recently been studied by potentiodynamic and potentiostatic testing in a 2N H₂SO₄ solution. As shown in Figure 9 nanocrystalline nickel exhibits the same active-passive-transpassive behaviour as observed in normal crystalline nickel. However the current density in the passive range for nanocrystalline materials is higher than for conventional nickel. This is believed to be due to the increased defect concentration in the passive layer on nanocrystalline material. On the other hand, nanoprocessed Ni did not show the detrimental type of localized corrosion along the grain boundaries which is usually observed for conventional nickel. Therefore, although the general corrosion rate is somewhat enhanced, the overall excellent corrosion performance of nickel is likely not sacrificed by nanoprocessing.

Thus using the invention it is possible to provide na-

nanocrystalline metals, binary, ternary and quaternary alloys having a grain size of less than 100 nm and some of which have enhanced magnetic properties.

Claims

1. A process for electrodepositing a selected metallic material in nanocrystalline form on a substrate in which an aqueous, electrolyte containing ions of said selected metallic material is introduced into an electrolytic cell having an anode and a cathode, while maintaining said electrolyte at a temperature in the range between about 15° and about 75°C, characterised by passing a D.C. current, having a peak current density in the range between about 0.1 and about 3.0 A/cm², at pulsed intervals during which said current passes for a time period in the range of about 0.1 to about 50 milliseconds and does not pass for a time period in the range of about 1 to about 500 milliseconds, between said anode and said cathode so as to deposit said selected metallic material in nanocrystalline form and having a grain size of less than 100 nm on said cathode.
2. A process as claimed in claim 1, characterised in that said selected metallic material is (a) a pure metal selected from the group consisting of Co, Cr, Cu, Fe, or (b) alloys containing at least two elements selected from Ni, Fe, Co, Zn, W, Cr, Cu, Mo, Mn, V, Si, P, C, and S, with the proviso that, in a binary alloy when a first said element is nickel, the second element is not iron or phosphorous and in a binary alloy in which the first element Co, the second element is not W.
3. A process as claimed in Claim 1 or Claim 2, characterised by maintaining said electrolyte at a temperature in the range between about 55° and about 75° and further characterised in that said peak current density is in the range between about 1.0 and about 3.0 A/cm², at pulsed intervals during which said current passes for a time period in the range of about 1.0 to about 5 milliseconds and does not pass for a time period in the range of about 30 to about 50 milliseconds.
4. A process as claimed in claim 3, characterised in that said selected metallic material is nickel.
5. A process as claimed in claim 3, characterised in that said anode is selected from nickel, platinum and graphite.
6. A process as claimed in claim 5, characterised in that said cathode is selected from titanium, steel, brass, copper, nickel, and graphite.
7. A process as claimed in claim 6, characterised in that said electrolyte additionally contains up to about 10g/l of a stress reliever and grain refining agent.
8. A process as claimed in claim 7, characterised in that said stress reliever and grain refining agent is selected from saccharin, coumarin sodium lauryl sulfate and thiourea.
9. A process as claimed in claim 8, characterised in that said electrolyte additionally contains a grain size inhibitor.
10. A process as claimed in claim 9, characterised in that said grain size inhibitor is phosphorous acid.
11. A process as claimed in claim 3, characterised in that said current passes for periods between 1.5 and 3.0 milliseconds and does not pass for a period between 40 and 50 milliseconds.
12. A process as claimed in claim 1, characterised by a step of periodic pulse reversal.
13. A process as claimed in claim 11, characterised in that said bath is maintained at a temperature in the range 60-70°C.
14. A process as claimed in claim 12, characterised in that said current passes for 2.5m sec and does not pass for 45m sec.
15. A process as claimed in claim 13, characterised in that said bath is maintained at a temperature of 65°C.
16. A process as claimed in claim 11, characterised in that said peak current density is in the range 1.5 - 2.2 A/cm².
17. A process as claimed in claim 16, characterised by a peak current density of about 1.9 A/cm².
18. A nanocrystalline nickel material, characterised by an average grain size of less than 11 nanometres and by a hardness which is at a maximum in a size range of 8 - 10 nm, and by saturation magnetization properties substantially equal to those of said nickel material in normal crystalline form.
19. A nanocrystalline metallic material having a grain size of less than 100 nm characterised by selection from the group consisting of (a) a pure metal selected from the group consisting of Co, Cr, Cu, and Fe, and (b) alloys containing at least two elements selected from the group consisting of Ni, Fe, Co, Zn, Ti, Mg, W, Cr, Cu, Mo, Mn, V, Si, P, C, and S, and

further characterised in a binary alloy in which a first said element is Ni, the second element is not Fe or P; and in a binary alloy in which the first element is Co, the second element is not W.

20. A nanocrystalline ternary or quaternary nickel-iron alloy having a grain size of less than 100 nm and characterized in that it is of the Ni Fe X₁ X₂ type where X₁ and X₂ are the same or different and selected from the group consisting of Cr, Co, Cu, Mo, Mn, V, Ti, Mg, Si, P, C, and S.
21. A nanocrystalline alloy as claimed in claim 20, characterised in that X₁ and X₂ are selected from Cr and Mn.
22. A nanocrystalline alloy as claimed in claim 20, characterised in that X₁ and X₂ are selected from Cr and Mo.
23. A nanocrystalline alloy as claimed in claim 20, characterised in that X₁ and X₂ are selected from Mo and Mn.
24. A nanocrystalline alloy as claimed in claim 20, characterised in that X₁ and X₂ are selected from Cu and Cr.
25. A process as claimed in claim 1, characterised in that said electrolyte includes up to 10g/l of a stress reliever and grain refining agent selected from the group consisting of saccharin, sodium citrate, EDTA, citric acid, sodium fluoride, coumarin, sodium lauryl sulfate and thiourea.
26. A process as claimed in claim 3, characterised by a step of periodic pulse reversal.

Patentansprüche

1. Verfahren zum elektrochemischen Abscheiden eines ausgewählten metallischen Materials in nanokristalliner Form auf einem Substrat, in welchem Verfahren in eine elektrolytische Zelle, die eine Anode und eine Kathode aufweist, ein wässriger Elektrolyt eingeführt wird, der Ionen dieses ausgewählten metallischen Materials enthält, während der Elektrolyt bei einer Temperatur im Bereich von etwa 15°C bis etwa 75°C gehalten wird, dadurch gekennzeichnet, daß ein Gleichstrom mit einer maximalen Stromdichte von etwa 0,1 bis etwa 3,0 A/cm² in gepulsten Intervallen hindurchgeleitet wird, währenddessen der Strom zwischen der Anode und der Kathode für eine Zeitdauer im Bereich von etwa 0,1 bis etwa 50 Millisekunden fließt und für eine Zeitdauer im Bereich von etwa 1 bis etwa 500 Millisekunden nicht fließt, um so das ausgewählte metal-

lische Material in nanokristalliner Form mit einer Korngröße von weniger als 100 nm auf der Kathode abzuscheiden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das ausgewählte metallische Material (a) ein reines Metall ist, ausgewählt aus der Gruppe, bestehend aus Co, Cr, Cu, Fe oder (b) Legierungen, enthaltend mindestens zwei Elemente, ausgewählt aus der Gruppe, bestehend aus Ni, Fe, Co, Zn, W, Cr, Cu, Mo, Mn, V, Si, P, C und S, und zwar unter der Voraussetzung, daß in einer binären Legierung, wenn das erste dieser Elemente Nickel ist, das zweite Element nicht Eisen oder Phosphor ist, und in einer binären Legierung, in der das erste Element Co ist, das zweite Element nicht W ist.
3. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß der Elektrolyt bei einer Temperatur im Bereich zwischen etwa 55°C und 75°C gehalten wird, und ferner dadurch gekennzeichnet, daß die maximale Stromdichte im Bereich zwischen etwa 1,0 und 3,0 A/cm² liegt und zwar bei gepulsten Intervallen, währenddessen der Strom für eine Zeitdauer im Bereich von etwa 1,0 bis etwa 5 Millisekunden fließt und für eine Zeitdauer im Bereich von etwa 30 bis etwa 50 Millisekunden nicht fließt.
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das ausgewählte metallische Material Nickel ist.
5. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die Anode ausgewählt wird aus Nickel, Platin und Graphit.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die Kathode ausgewählt wird aus Titan, Stahl, Messing, Kupfer, Nickel und Graphit.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß der Elektrolyt zusätzlich bis zu etwa 10 g/l ein Mittel zum Spannungsverringern und zur Kornverfeinerung enthält.
8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Mittel zum Spannungsverringern und zur Kornverfeinerung ausgewählt wird aus Saccharin, Coumarin, Natriumlaurylsulfat und Thioharnstoff.
9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß der Elektrolyt zusätzlich einen Korngrößeninhibitor enthält.
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß der Korngrößeninhibitor Phosphorsäure ist.

11. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Strom für eine Zeitdauer zwischen 1,5 und 3,0 Millisekunden fließt und für eine Zeitdauer zwischen 40 und 50 Millisekunden nicht fließt.
12. Verfahren nach Anspruch 1, gekennzeichnet durch einen Schritt der periodischen Pulsumkehr.
13. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Bad bei einer Temperatur im Bereich von 60° bis 70°C gehalten wird.
14. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß der Strom für 2,5 Millisekunden fließt und für 45 Millisekunden nicht fließt.
15. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Bad bei einer Temperatur von 65°C gehalten wird.
16. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß die maximale Stromdichte im Bereich von 1,5 bis 2,2 A/cm² liegt.
17. Verfahren nach Anspruch 16, gekennzeichnet durch eine maximale Stromdichte von etwa 1,9 A/cm².
18. Nanokristallines Material aus Nickel, gekennzeichnet durch eine mittlere Korngröße von weniger als 11 Nanometern und durch eine Härte mit einem Maximum bei 8 bis 10 nm sowie durch Eigenschaften der Sättigungsmagnetsierung, die im wesentlichen gleich denen des Nickelmaterials in normaler kristalliner Form sind.
19. Nanokristallines metallisches Material mit einer Korngröße von weniger als 100 nm, gekennzeichnet durch die Auswahl aus der Gruppe, bestehend aus (a) einem reinen Metall, ausgewählt aus der Gruppe, bestehend aus Co, Cr, Cu und Fe, und (b) Legierungen, enthaltend mindestens zwei Elemente, ausgewählt aus der Gruppe, bestehend aus Ni, Fe, Co, Zn, Ti, Mg, W, Cr, Cu, Mo, Mn, V, Si, P, C und S, und ferner gekennzeichnet durch eine binäre Legierung, in der das erste dieser Elemente Nickel ist, das zweite Element nicht Eisen oder Phosphor ist; und in einer binären Legierung, in der das erste Element Co ist und das zweite Element nicht W ist.
20. Nanokristallines ternäre oder quaternäre Nickel-Eisen-Legierung mit einer Korngröße von weniger als 100 nm und dadurch gekennzeichnet, daß sie vom Ni/Fe/X₁/X₂-Typ ist, worin X₁ und X₂ gleich oder verschieden sind und ausgewählt werden aus der Gruppe, bestehend aus Cr, Co, Cu, Mo, Mn, V, Ti, Mg, Si, P, C und S.

21. Nanokristallines Legierung nach Anspruch 20, dadurch gekennzeichnet, daß X₁ und X₂ ausgewählt werden aus Cr und Mn.
22. Nanokristallines Legierung nach Anspruch 20, dadurch gekennzeichnet, daß X₁ und X₂ ausgewählt werden aus Cr und Mo.
23. Nanokristallines Legierung nach Anspruch 20, dadurch gekennzeichnet, daß X₁ und X₂ ausgewählt werden aus Mo und Mn.
24. Nanokristallines Legierung nach Anspruch 20, dadurch gekennzeichnet, daß X₁ und X₂ ausgewählt werden aus Cu und Cr.
25. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Elektrolyt bis zu 10 g/l Mittel zum Spannungsverringern und zur Kornverfeinerung einschließt, ausgewählt aus der Gruppe, bestehend aus Saccharin, Natriumcitrat, EDTA, Citronensäure, Natriumfluorid, Cumarin, Natriumlaurylsulfat und Thioharnstoff.
26. Verfahren nach Anspruch 3, gekennzeichnet durch den Schritt der periodischen Pulsumkehr.

Revendications

1. Procédé pour le dépôt électrolytique d'un matériau métallique sélectionné, sous forme nanocristalline sur un substrat, dans lequel un électrolyte aqueux contenant des ions dudit matériau métallique sélectionné est introduit à l'intérieur d'une cellule d'électrolyse comportant une anode et une cathode, tout en maintenant ledit électrolyte à une température comprise entre environ 15°C et environ 75°C, caractérisé par le fait de faire passer un courant continu, de densité de courant maximale comprise entre environ 0,1 et environ 3,0 A/cm², à intervalles pulsés durant lesquels ledit courant passe pendant une durée comprise entre environ 0,1 et environ 50 millisecondes et ne passe pas pendant une durée comprise entre environ 1 et environ 500 millisecondes, entre ladite anode et ladite cathode afin de déposer sous forme nanocristalline ledit matériau métallique sélectionné dont les grains ont une grosseur inférieure à 100 nm sur ladite cathode.
2. Procédé selon la revendication 1, caractérisé en ce que ledit matériau métallique sélectionné consiste en (a) un métal pur choisi dans le groupe constitué de Co, de Cr, de Cu, de Fe, ou (b) des alliages contenant au moins deux éléments choisis parmi Ni, Fe, Co, Zn, W, Cr, Cu, Mo, Mn, V, Si, P, C, et S, à la condition que, dans un alliage binaire où ledit premier élément est le nickel, le second élément ne soit

pas le fer ou le phosphore et que dans un alliage binaire dans lequel ledit premier élément est Co, le second élément ne soit pas W.

3. Procédé selon la revendication 1 ou 2, caractérisé par le fait de maintenir ledit électrolyte à une température comprise entre environ 55°C et environ 75°C et caractérisé en outre en ce que ladite densité de courant maximale est comprise entre environ 1,0 et environ 3,0 A/cm², à intervalles pulsés durant lesquels ledit courant passe pendant une durée comprise entre environ 1,0 et environ 5 millisecondes et ne passe pas pendant une durée comprise entre environ 30 et environ 50 millisecondes.
4. Procédé selon la revendication 3, caractérisé en ce que ledit matériau métallique sélectionné est le nickel.
5. Procédé selon la revendication 3, caractérisé en ce que ladite anode est choisie parmi le nickel, le platine et le graphite.
6. Procédé selon la revendication 5, caractérisé en ce que ladite cathode est choisie parmi le titane, l'acier, le laiton, le cuivre, le nickel, et le graphite.
7. Procédé selon la revendication 6, caractérisé en ce que ledit électrolyte contient en plus jusqu'à environ 10 g/l d'un agent de stabilisation et d'affinage de grains.
8. Procédé selon la revendication 7, caractérisé en ce que ledit agent de stabilisation et d'affinage de grains est choisi parmi la saccharine, la coumarine, le laurylsulfate de sodium et la thiourée.
9. Procédé selon la revendication 8, caractérisé en ce que ledit électrolyte contient en plus un inhibiteur granulométrique.
10. Procédé selon la revendication 9, caractérisé en ce que ledit inhibiteur granulométrique est l'acide phosphoreux.
11. Procédé selon la revendication 3, caractérisé en ce que ledit courant passe pendant des périodes comprises entre 1,5 et 3,0 millisecondes et ne passe pas pendant une période comprise entre 40 et 50 millisecondes.
12. Procédé selon la revendication 1, caractérisé par une étape d'inversion périodique des impulsions.
13. Procédé selon la revendication 11, caractérisé en ce que ledit bain est maintenu à une température de 60 à 70°C.

14. Procédé selon la revendication 12, caractérisé en ce que ledit courant passe pendant 2,5 msec et ne passe pas pendant 45 msec.

15. Procédé selon la revendication 13, caractérisé en ce que ledit bain est maintenu à une température de 65°C.

16. Procédé selon la revendication 11, caractérisé en ce que ladite densité de courant maximale est comprise entre 1,5 et 2,2 A/cm².

17. Procédé selon la revendication 16, caractérisé par une densité de courant maximale d'environ 1,9 A/cm².

18. Matériau en nickel nanocristallin, caractérisé par une grosseur moyenne de grains inférieure à 11 nanomètres et par une dureté qui a une étendue granulométrique au maximum comprise entre 8 et 10 nm, et par des caractéristiques de saturation magnétique pratiquement égales à celles dudit matériau en nickel sous forme cristalline normale.

19. Matériau métallique nanocristallin dont les grains ont une grosseur inférieure à 100 nm caractérisé par sélection dans le groupe constitué (a) d'un métal pur choisi dans le groupe constitué de Co, de Cr, de Cu, de Fe, et (b) d'alliages contenant au moins deux éléments choisis parmi Ni, Fe, Co, Zn, Ti, Mg, W, Cr, Cu, Mo, Mn, V, Si, P, C, et S, et caractérisé en outre par le fait que, dans un alliage binaire dans lequel un premier dit élément est Ni, le second élément n'est ni Fe ni P; et dans un alliage binaire dans lequel le premier élément est Co, le second élément n'est pas W.

20. Alliage nanocristallin nickel/fer, ternaire ou quaternaire, dont les grains ont une grosseur inférieure à 100 nm et caractérisé en ce qu'il est du type Ni Fe X₁ X₂ où X₁ et X₂ sont identiques ou différents et choisis dans le groupe constitué de Cr, de Co, de Cu, de Mo, de Mn, de V, de Ti, de Mg, de Si, de P, de C, et de S.

21. Alliage nanocristallin selon la revendication 20, caractérisé en ce que X₁ et X₂ sont choisis parmi Cr et Mn.

22. Alliage nanocristallin selon la revendication 20, caractérisé en ce que X₁ et X₂ sont choisis parmi Cr et Mo.

23. Alliage nanocristallin selon la revendication 20, caractérisé en ce que X₁ et X₂ sont choisis parmi Mo et Mn.

24. Alliage nanocristallin selon la revendication 20, ca-

ractérisé en ce que X_1 et X_2 sont choisis parmi Cu et Cr.

25. Procédé selon la revendication 1, caractérisé en ce que l'électrolyte comprend jusqu'à 10 g/l d'un agent de stabilisation et d'affinage de grains choisi dans le groupe constitué de la saccharine, du citrate de sodium, de l'EDTA, de l'acide citrique, du fluorure de sodium, de la coumarine, du laurylsulfate de sodium et de la thiourée.

26. Procédé selon la revendication 3, caractérisé par une étape d'inversion périodique des impulsions.

15

20

25

30

35

40

45

50

55

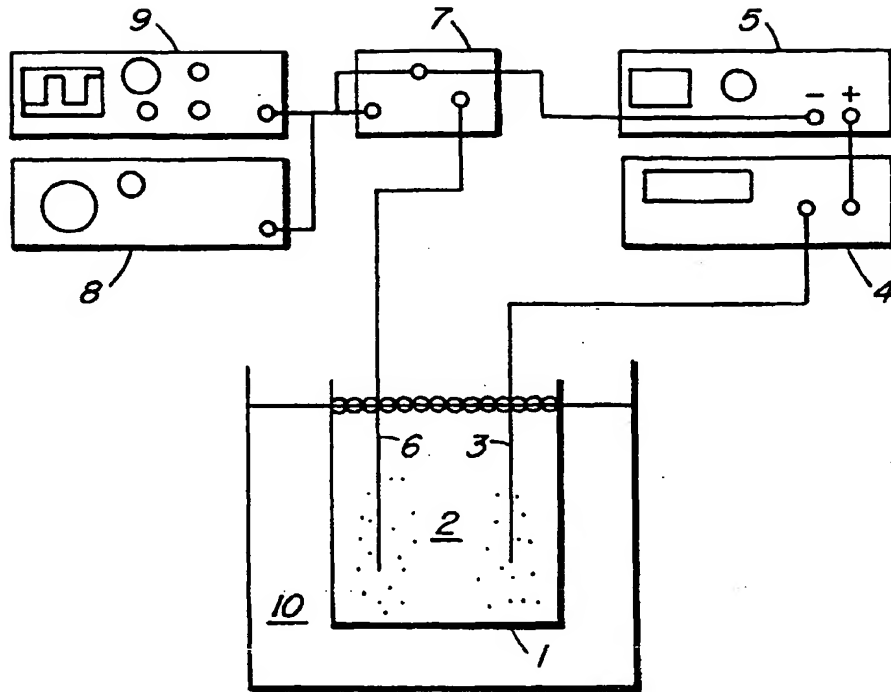


FIG. 1

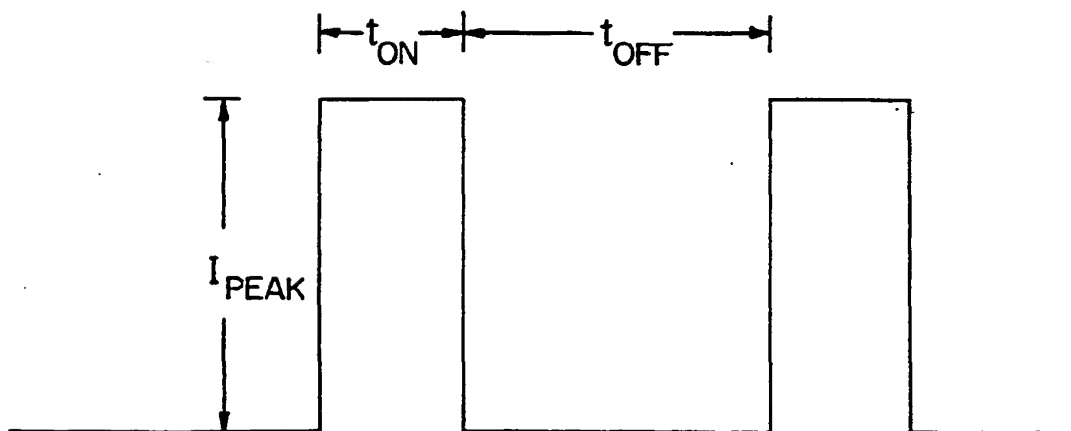


FIG. 2

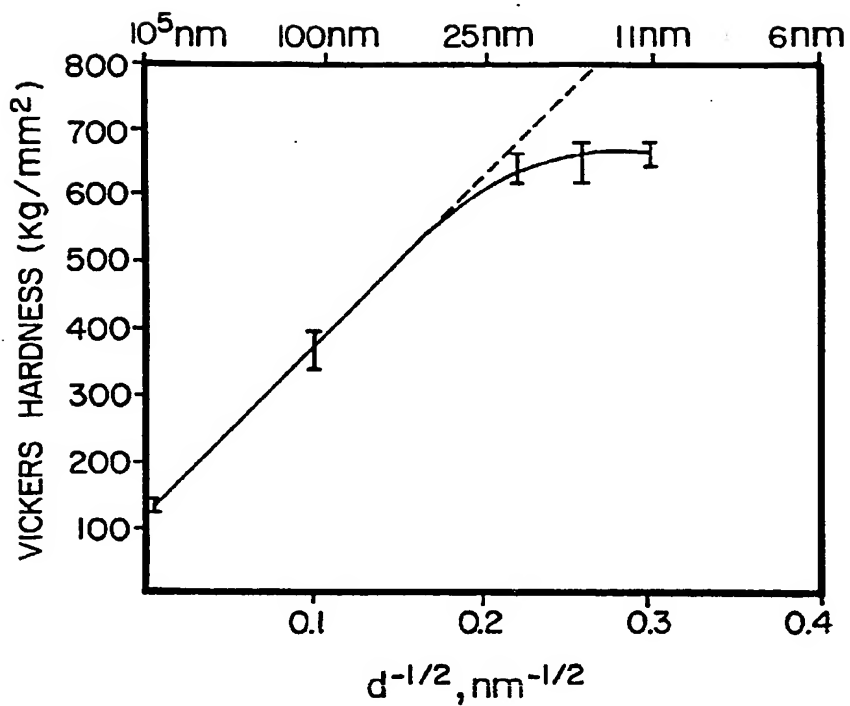


FIG. 3

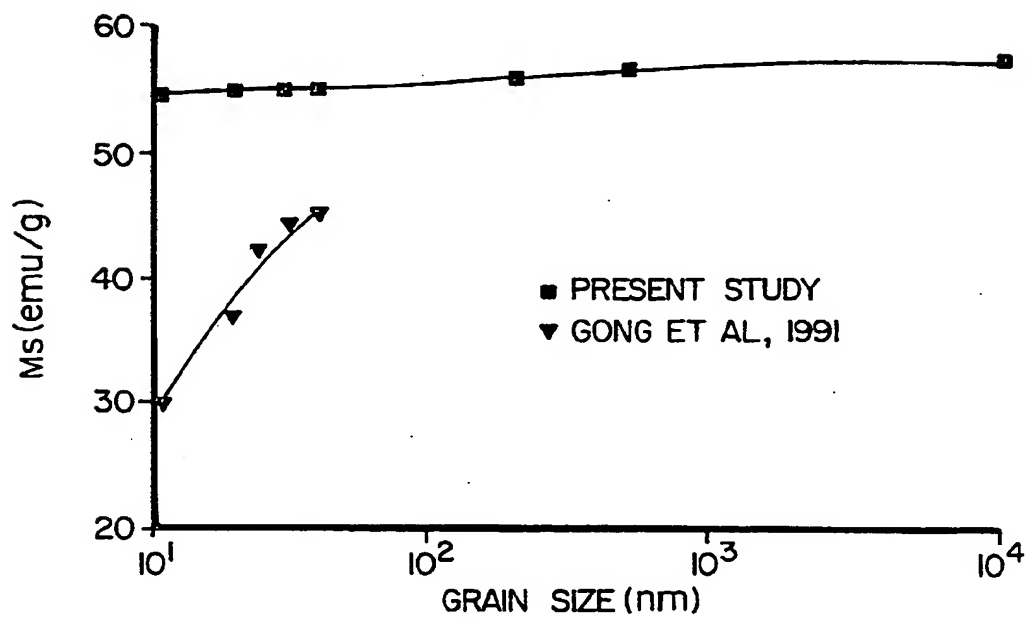


FIG. 4

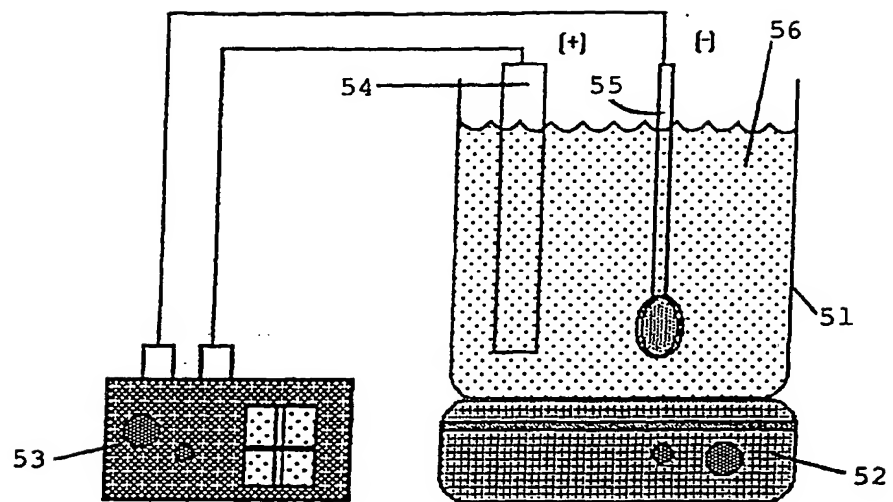


FIGURE 5

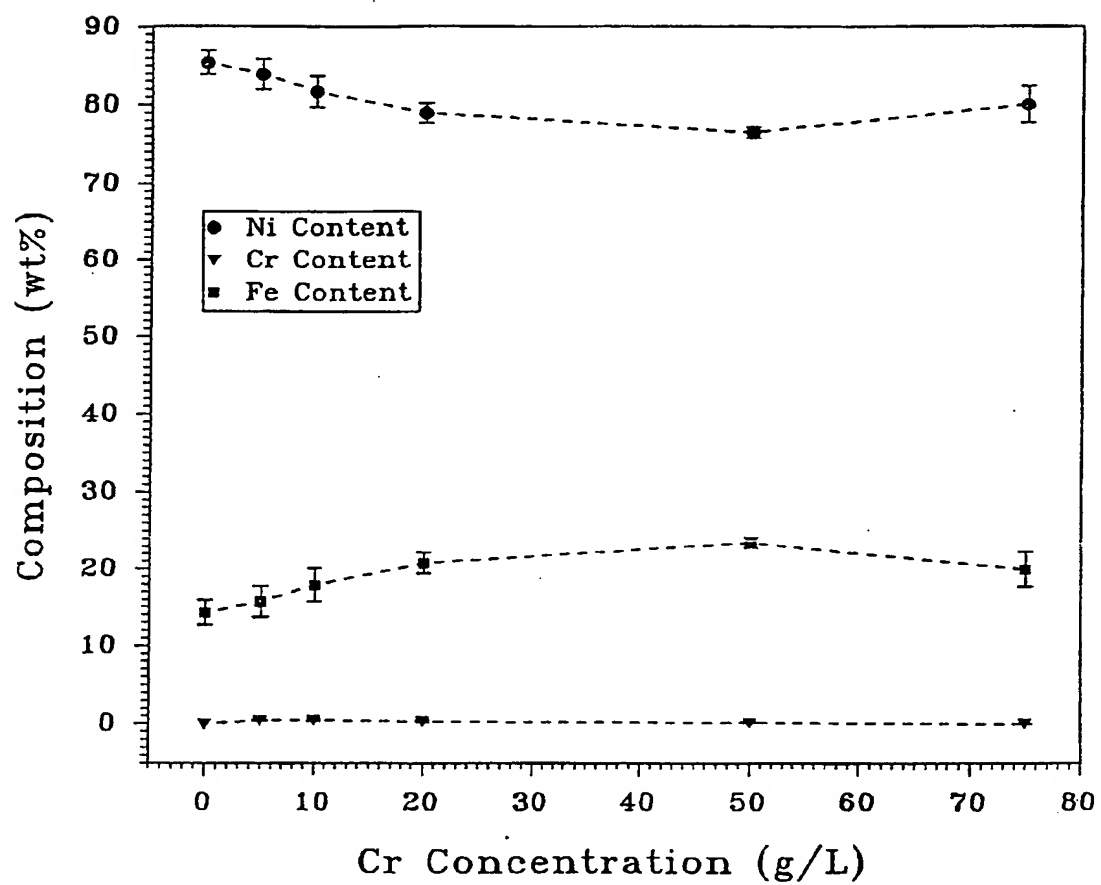


FIGURE 6

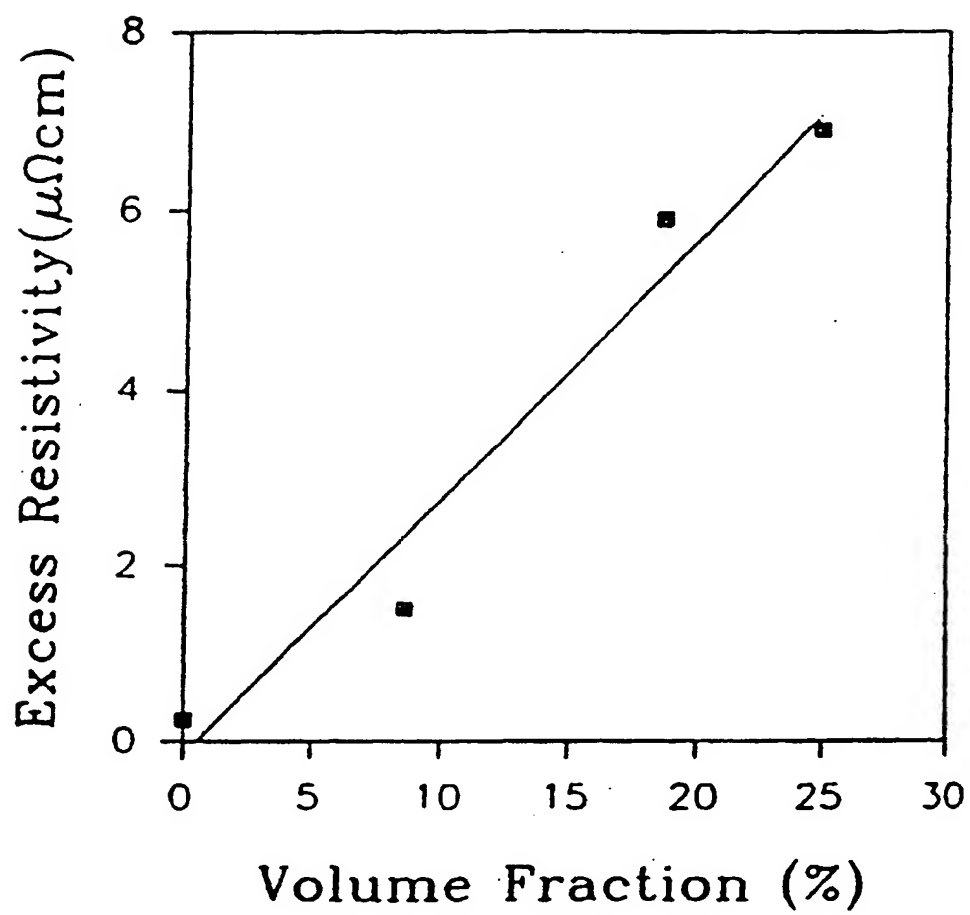


FIGURE 7

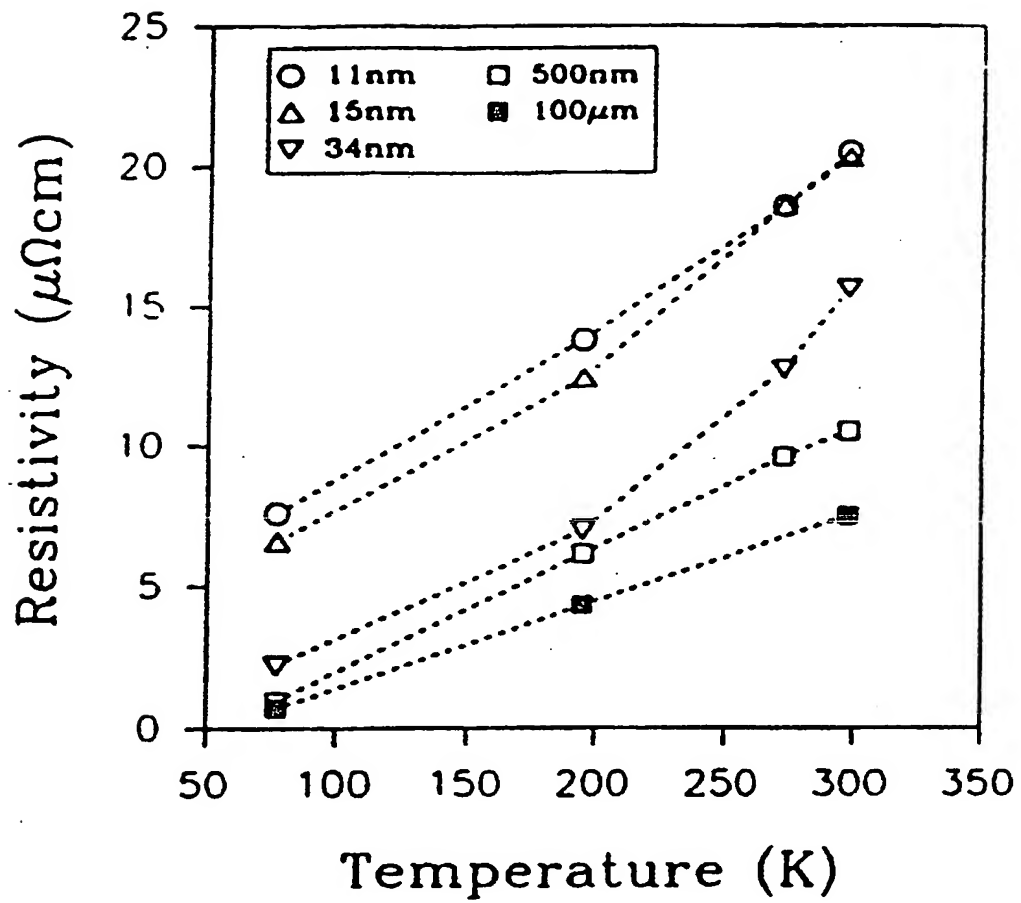


FIGURE 8

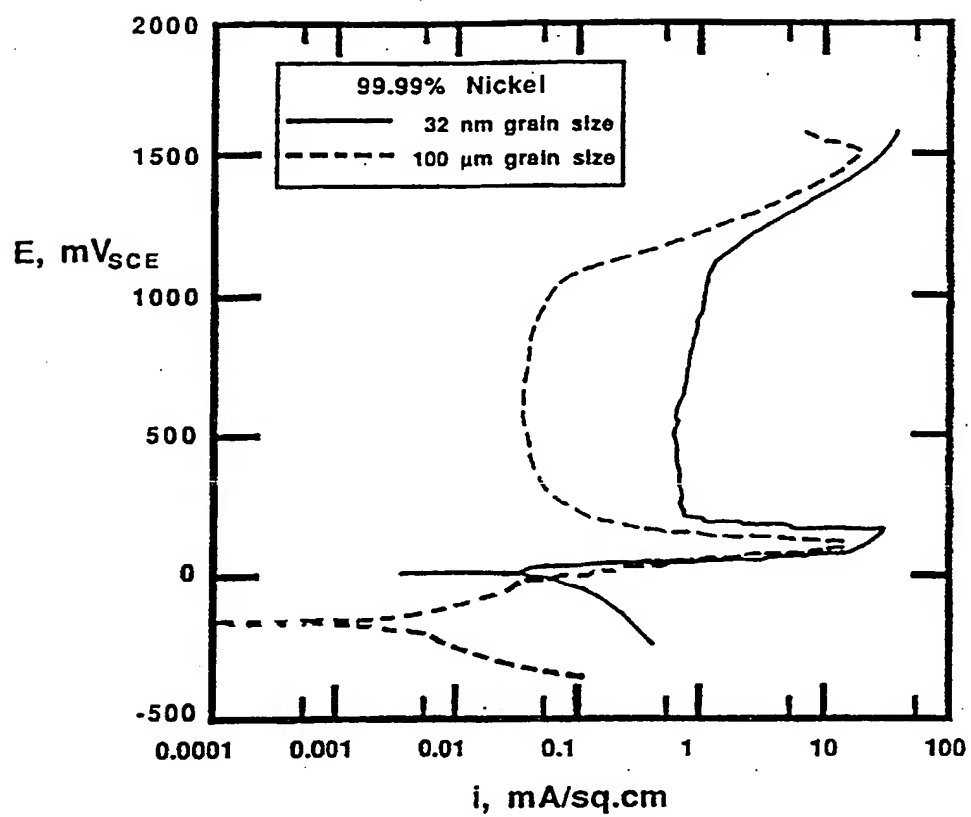


FIGURE 9